Supporting Information for：

Theoretical insights into the gaseous and heterogeneous reactions of halogenated phenols with ·OH radical: Mechanism, kinetics, and role of $(TiO_2)_n$ clusters in degradation processes

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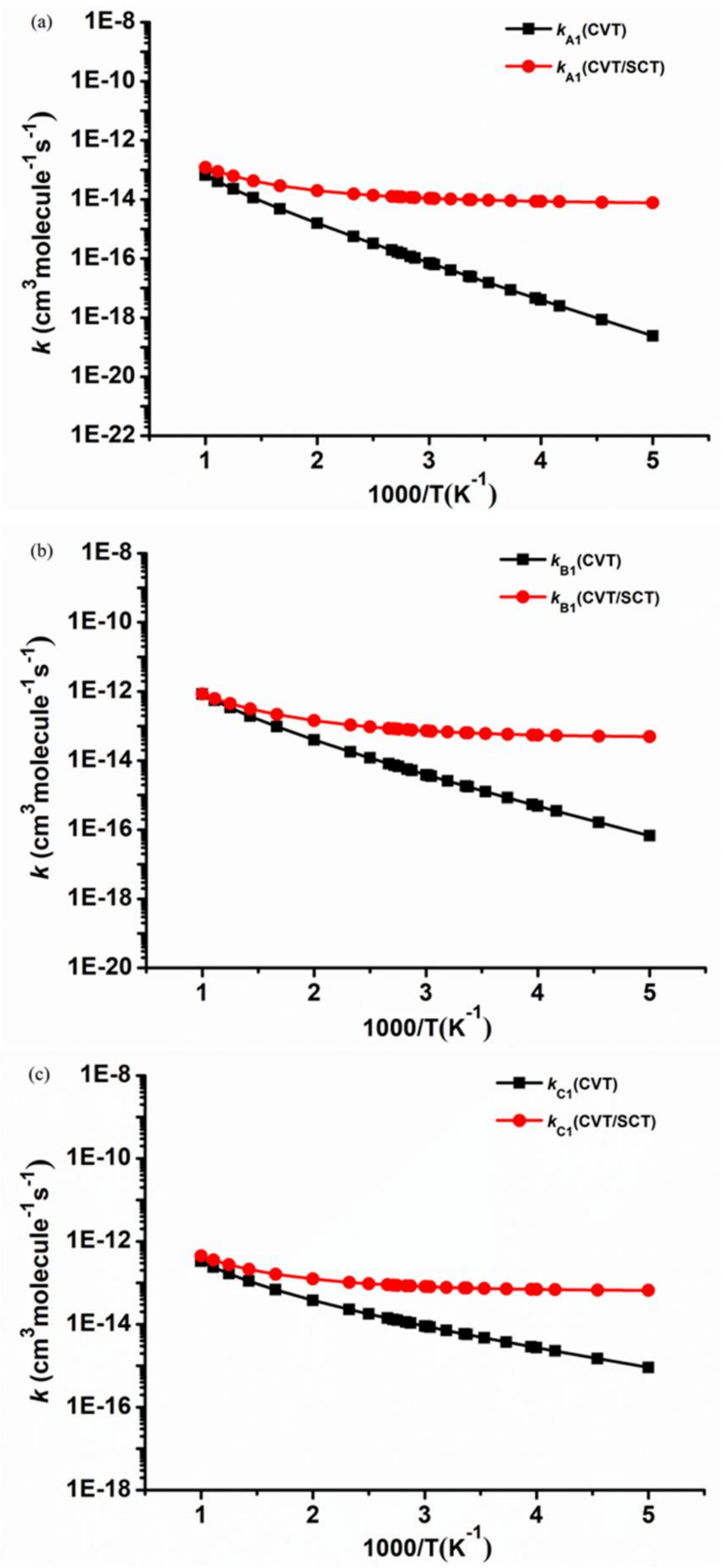


Figure S1. The CVT and CVT/SCT values for the individual reactions of C_6X_5OH (X=F, Cl, and Br) with ·OH radical at the CCSD(T)/aug-cc-pVDZ//M06-2X/6-311G(d,p) level.

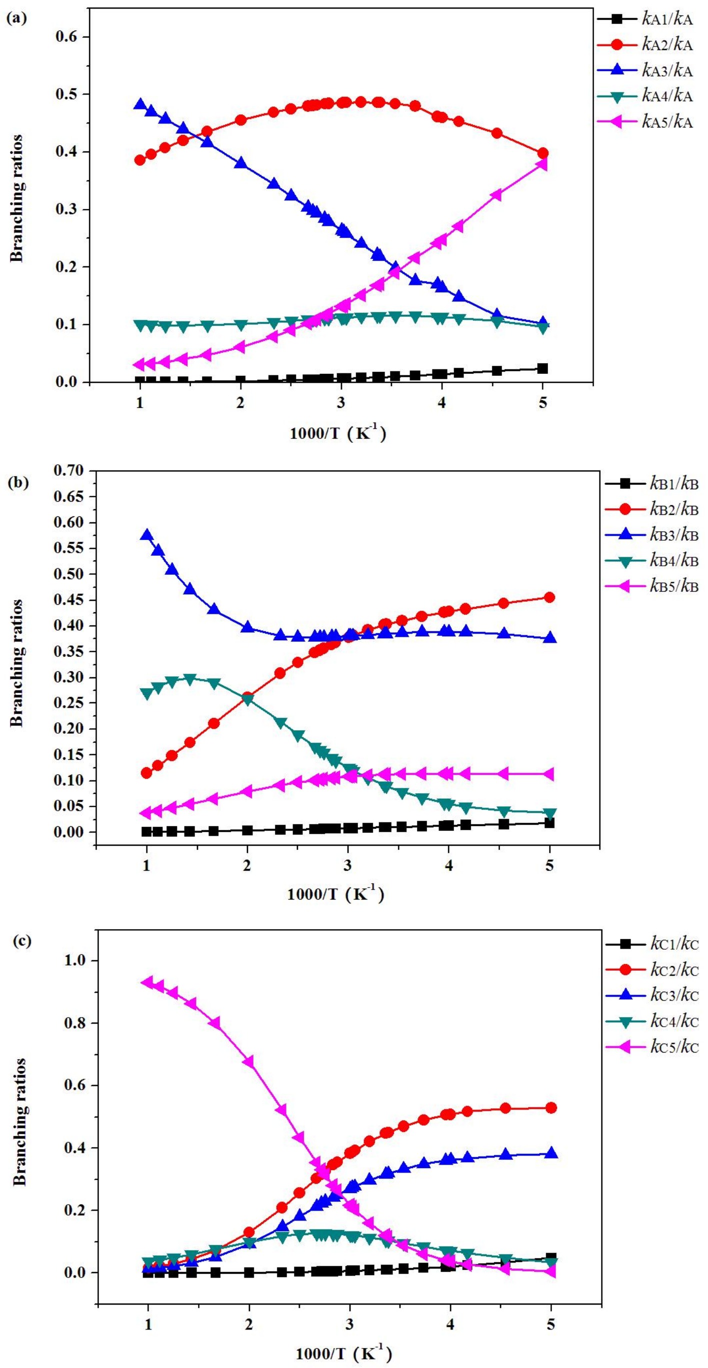
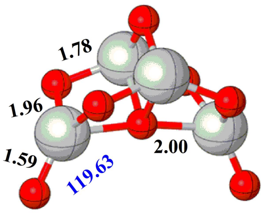
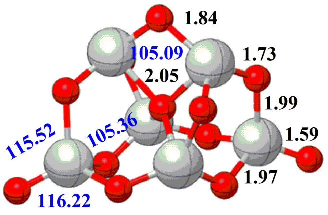


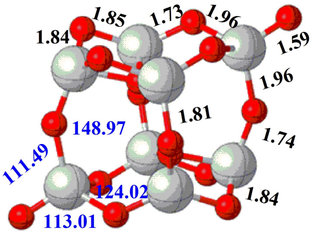
Figure S2. The branching ratios of rate coefficients versus 1000/T for the individual reactions of C_6X_5OH (X=F, Cl, and Br) with ·OH radical at the CCSD(T)/aug-cc-pVDZ//M06-2X/6-311G(d,p) level.



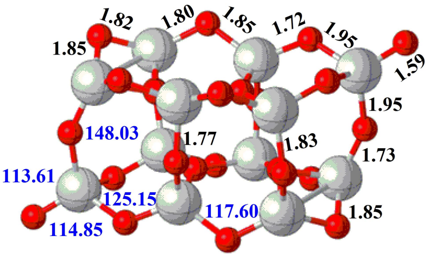
$(TiO_2)_4$



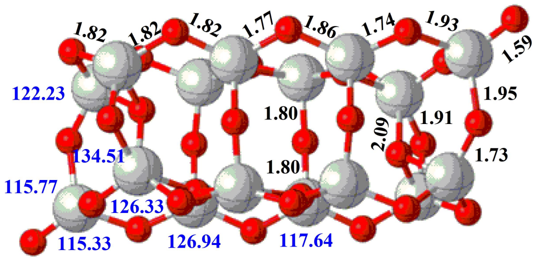
$(TiO_2)_6$



$(TiO_2)_8$

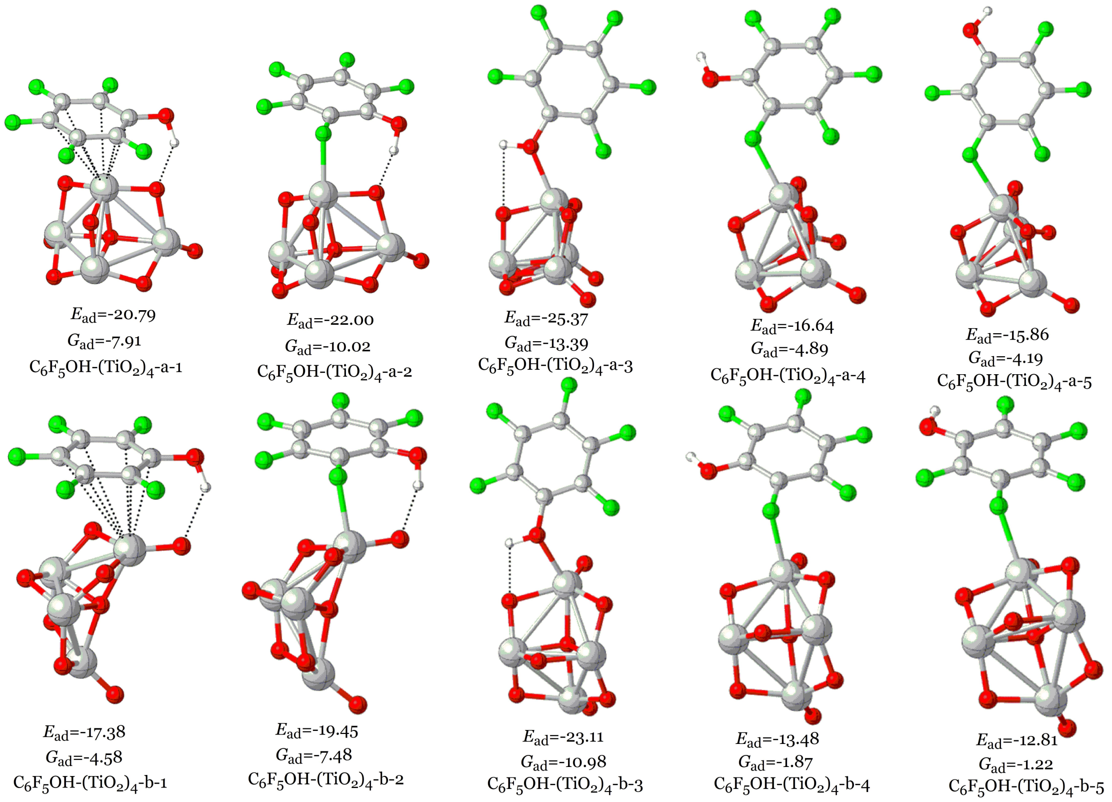


$(TiO_2)_{12}$



$(TiO_2)_{16}$

Figure S3. The structures parameters of $(TiO_2)_n$ (n=4, 6, 8, 12, and 16) obtained at the M06-2X/6-311G(d,p)/LANL2DZ level.



E_{ad}=-20.79
G_{ad}=-7.91
$C_6F_5OH-(TiO_2)_4$-a-1

E_{ad}=-22.00
G_{ad}=-10.02
$C_6F_5OH-(TiO_2)_4$-a-2

E_{ad}=-25.37
G_{ad}=-13.39
$C_6F_5OH-(TiO_2)_4$-a-3

E_{ad}=-16.64
G_{ad}=-4.89
$C_6F_5OH-(TiO_2)_4$-a-4

E_{ad}=-15.86
G_{ad}=-4.19
$C_6F_5OH-(TiO_2)_4$-a-5

E_{ad}=-17.38
G_{ad}=-4.58
$C_6F_5OH-(TiO_2)_4$-b-1

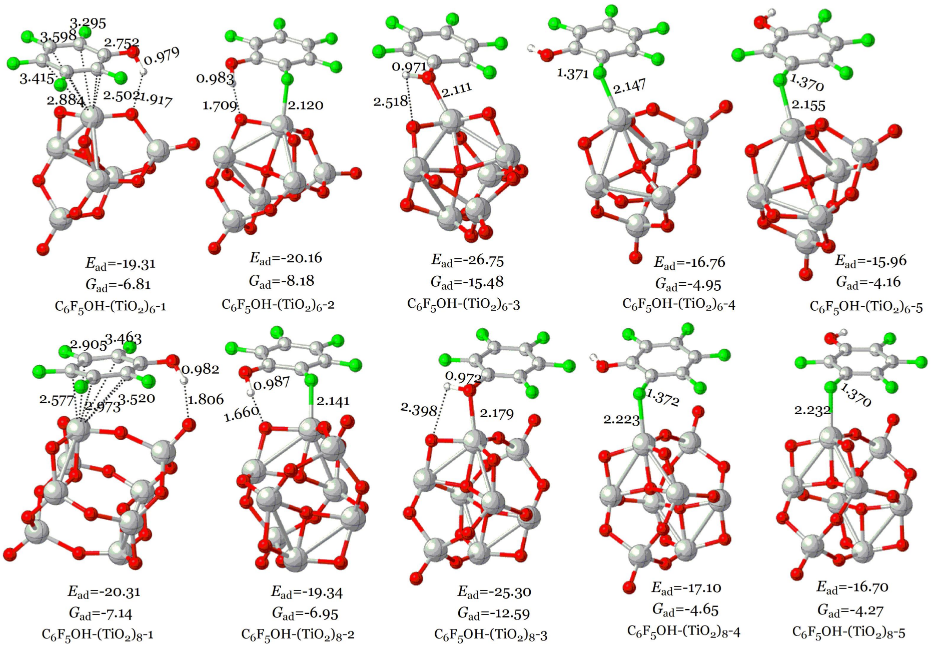
E_{ad}=-19.45
G_{ad}=-7.48
$C_6F_5OH-(TiO_2)_4$-b-2

E_{ad}=-23.11
G_{ad}=-10.98
$C_6F_5OH-(TiO_2)_4$-b-3

E_{ad}=-13.48
G_{ad}=-1.87
$C_6F_5OH-(TiO_2)_4$-b-4

E_{ad}=-12.81
G_{ad}=-1.22
$C_6F_5OH-(TiO_2)_4$-b-5

Figure S4. Feasible adsorption configurations of C_6F_5OH onto two different central Ti (a and b) of $(TiO_2)_4$ cluster surface along with corresponding adsorption energies (E_{ad}) and adsorption free energies (ΔG) (in kcal/mol).



E_{ad}=-19.31
G_{ad}=-6.81
C_6F_5OH-$(TiO_2)_6$-1

E_{ad}=-20.16
G_{ad}=-8.18
C_6F_5OH-$(TiO_2)_6$-2

E_{ad}=-26.75
G_{ad}=-15.48
C_6F_5OH-$(TiO_2)_6$-3

E_{ad}=-16.76
G_{ad}=-4.95
C_6F_5OH-$(TiO_2)_6$-4

E_{ad}=-15.96
G_{ad}=-4.16
C_6F_5OH-$(TiO_2)_6$-5

E_{ad}=-20.31
G_{ad}=-7.14
C_6F_5OH-$(TiO_2)_8$-1

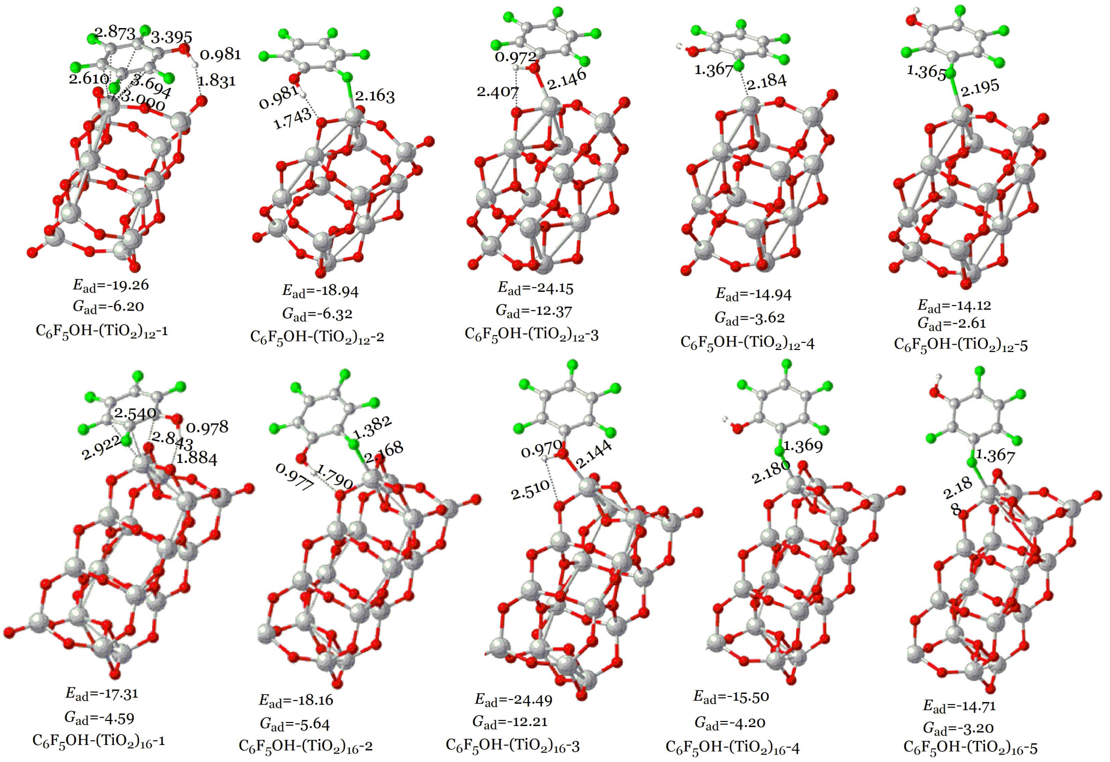
E_{ad}=-19.34
G_{ad}=-6.95
C_6F_5OH-$(TiO_2)_8$-2

E_{ad}=-25.30
G_{ad}=-12.59
C_6F_5OH-$(TiO_2)_8$-3

E_{ad}=-17.10
G_{ad}=-4.65
C_6F_5OH-$(TiO_2)_8$-4

E_{ad}=-16.70
G_{ad}=-4.27
C_6F_5OH-$(TiO_2)_8$-5

Figure S5. Feasible adsorption configurations of C_6F_5OH onto the surface of $(TiO_2)_6$ and $(TiO_2)_8$ clusters along with corresponding adsorption energies (E_{ad}) and adsorption free energies (ΔG) (in kcal/mol).



E_{ad}=-19.26
G_{ad}=-6.20
C_6F_5OH-$(TiO_2)_{12}$-1

E_{ad}=-18.94
G_{ad}=-6.32
C_6F_5OH-$(TiO_2)_{12}$-2

E_{ad}=-24.15
G_{ad}=-12.37
C_6F_5OH-$(TiO_2)_{12}$-3

E_{ad}=-14.94
G_{ad}=-3.62
C_6F_5OH-$(TiO_2)_{12}$-4

E_{ad}=-14.12
G_{ad}=-2.61
C_6F_5OH-$(TiO_2)_{12}$-5

E_{ad}=-17.31
G_{ad}=-4.59
C_6F_5OH-$(TiO_2)_{16}$-1

E_{ad}=-18.16
G_{ad}=-5.64
C_6F_5OH-$(TiO_2)_{16}$-2

E_{ad}=-24.49
G_{ad}=-12.21
C_6F_5OH-$(TiO_2)_{16}$-3

E_{ad}=-15.50
G_{ad}=-4.20
C_6F_5OH-$(TiO_2)_{16}$-4

E_{ad}=-14.71
G_{ad}=-3.20
C_6F_5OH-$(TiO_2)_{16}$-5

Figure S6. Feasible adsorption configurations of C_6F_5OH onto the surface of $(TiO_2)_{12}$ and $(TiO_2)_{16}$ clusters along with corresponding adsorption energies (E_{ad}) and adsorption free energies (ΔG) (in kcal/mol).

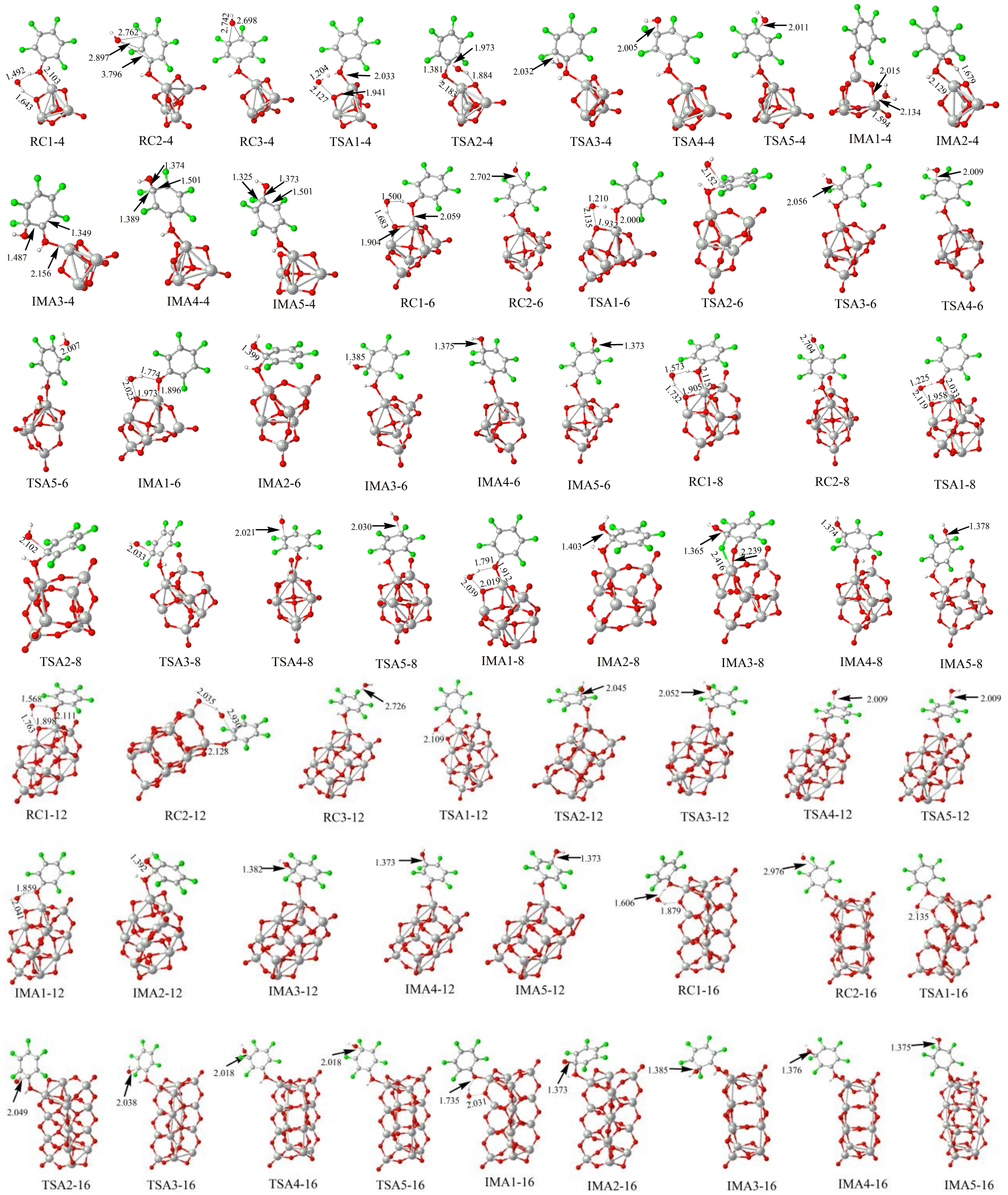


Figure S7. Optimized geometries of transition states and adsorption intermediates involved in the reactions of ·OH radical with C_6F_5OH onto the surface of $(TiO_2)_n$ (n=4, 6, 8, 12, and 16) clusters .

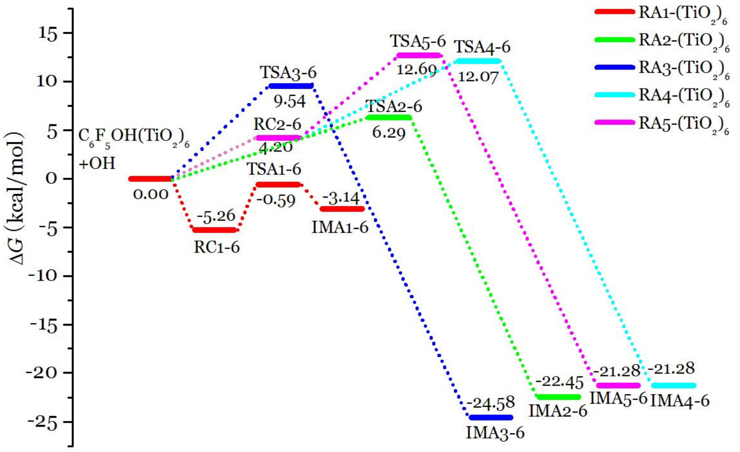


Figure S8. Schematic free energy surface for ·OH-initiated of C_6F_5OH catalyzed by $(TiO_2)_6$ cluster at the M06-2X/6-311++G(3df,3pd)-LANL2DZ//M06-2X/6-311G(d,p)-LANL2DZ level.

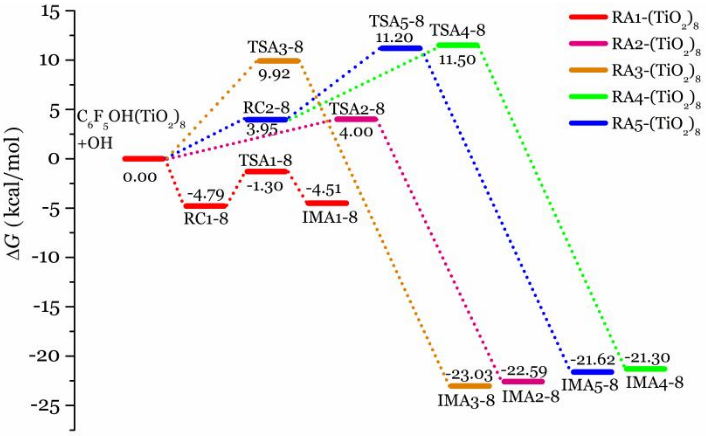


Figure S9. Schematic free energy surface for ·OH-initiated of C_6F_5OH catalyzed by $(TiO_2)_8$ cluster at the M06-2X/6-311++G(3df,3pd)-LANL2DZ//M06-2X/6-311G(d,p)-LANL2DZ level.

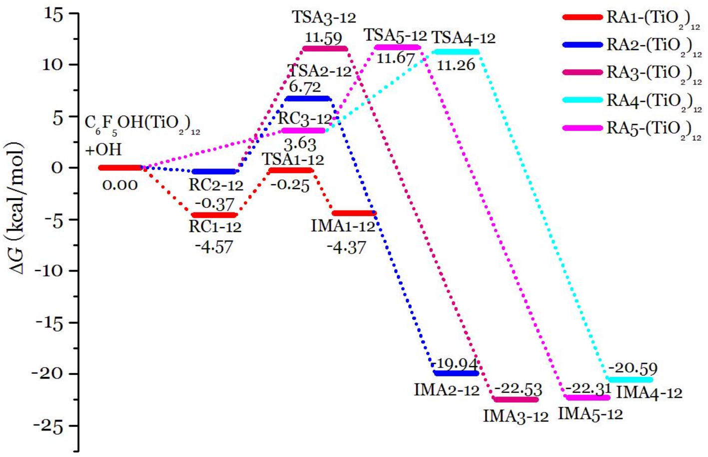


Figure S10. Schematic free energy surface for ·OH-initiated of C_6F_5OH catalyzed by $(TiO_2)_{12}$ cluster at the M06-2X/6-311++G(3df,3pd)-LANL2DZ//M06-2X/6-311G(d,p)-LANL2DZ level.

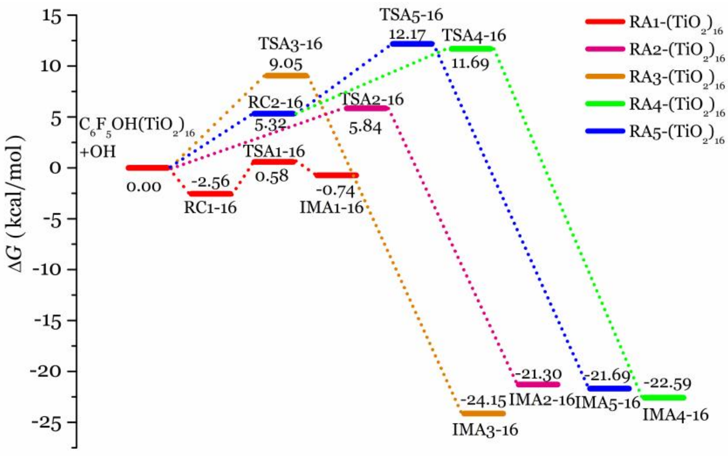


Figure S11. Schematic free energy surface for ·OH-initiated of C_6F_5OH onto $(TiO_2)_{16}$ clusters at the M06-2X/6-311++G(3df,3pd)-LANL2DZ//M06-2X/6-31G(d)-LANL2DZ level.

Table S1. Calculated individual and total CVT/SCT rate constants versus 1000/T along with the experimental values for reactions of C_6F_5OH with ·OH radical.

T (K)	k_{A1}	k_{A2}	k_{A3}	k_{A4}	k_{A5}	k_A	*Expt.*
200	4.45E-14	7.51E-13	1.94E-13	1.82E-13	7.16E-13	1.89E-12	
220	4.6E-14	1.01E-12	2.7E-13	2.49E-13	7.6E-13	2.33E-12	
240	4.79E-14	1.36E-12	4.44E-13	3.36E-13	8.14E-13	3.00E-12	
250	4.89E-14	1.57E-12	5.59E-13	3.87E-13	8.47E-13	3.41E-12	
253	4.92E-14	1.64E-12	6.06E-13	4.03E-13	8.58E-13	3.56E-12	
268	5.09E-14	2.03E-12	7.46E-13	4.92E-13	9.14E-13	4.23E-12	
283	5.28E-14	2.48E-12	1.02E-12	5.95E-13	9.76E-13	5.12E-12	
296	5.45E-14	2.93E-12	1.32E-12	6.96E-13	1.03E-12	6.03E-12	(6.88±1.37)E-12
298	5.48E-14	3.0E-12	1.37E-12	7.12E-13	1.04E-12	6.18E-12	
313	5.69E-14	3.6E-12	1.78E-12	8.45E-13	1.12E-12	7.40E-12	
328	5.91E-14	4.28E-12	2.27E-12	9.94E-13	1.2E-12	8.80E-12	
331	5.96E-14	4.42E-12	2.38E-12	1.03E-12	1.21E-12	9.10E-12	
333	5.99E-14	4.52E-12	2.46E-12	1.05E-12	1.23E-12	9.32E-12	
348	6.23E-14	5.31E-12	3.06E-12	1.22E-12	1.31E-12	1.09E-11	
353	6.32E-14	5.59E-12	3.29E-12	1.28E-12	1.34E-12	1.16E-11	
363	6.49E-14	6.18E-12	3.77E-12	1.41E-12	1.41E-12	1.28E-11	
368	6.58E-14	6.49E-12	4.02E-12	1.48E-12	1.44E-12	1.35E-11	
375	6.71E-14	6.94E-12	4.4E-12	1.58E-12	1.48E-12	1.45E-11	
400	7.18E-14	8.71E-12	5.94E-12	1.96E-12	1.66E-12	1.83E-11	
430	7.8E-14	1.12E-11	8.2E-12	2.51E-12	1.89E-12	2.39E-11	
500	9.45E-14	1.86E-11	1.55E-11	4.14E-12	2.51E-12	4.08E-11	
600	1.23E-13	3.3E-11	3.15E-11	7.54E-12	3.63E-12	7.58E-11	
700	1.59E-13	5.27E-11	5.51E-11	1.24E-11	5.05E-12	1.25E-10	
800	2.04E-13	7.78E-11	8.72E-11	1.89E-11	6.79E-12	1.91E-10	
900	2.59E-13	1.08E-10	1.28E-10	2.74E-11	8.88E-12	2.73E-10	
1000	3.25E-13	1.44E-10	1.8E-10	3.78E-11	1.14E-11	3.74E-10	

Table S2. Calculated individual and total CVT/SCT rate constants versus 1000/T for reactions of C_6Cl_5OH with·OH radical.

T (K)	k_{B1}	k_{B2}	k_{B3}	k_{B4}	k_{B5}	k_B
200	4.95E-14	1.25E-12	1.03E-12	1.06E-13	3.1E-13	2.75E-12
220	5.1E-14	1.42E-12	1.23E-12	1.37E-13	3.64E-13	3.20E-12
240	5.33E-14	1.64E-12	1.47E-12	1.91E-13	4.32E-13	3.79E-12
250	5.47E-14	1.77E-12	1.6E-12	2.3E-13	4.72E-13	4.13E-12
253	5.52E-14	1.81E-12	1.65E-12	2.44E-13	4.84E-13	4.24E-12
268	5.77E-14	2.03E-12	1.88E-12	3.26E-13	5.53E-13	4.85E-12
283	6.05E-14	2.28E-12	2.15E-12	4.37E-13	6.3E-13	5.56E-12
296	6.32E-14	2.53E-12	2.41E-12	5.62E-13	7.05E-13	6.27E-12
298	6.37E-14	2.57E-12	2.46E-12	5.84E-13	7.17E-13	6.39E-12
313	6.72E-14	2.88E-12	2.81E-12	7.74E-13	8.13E-13	7.34E-12
328	7.11E-14	3.23E-12	3.22E-12	1.01E-12	9.19E-13	8.45E-12
331	7.19E-14	3.3E-12	3.31E-12	1.07E-12	9.42E-13	8.69E-12
333	7.25E-14	3.35E-12	3.37E-12	1.11E-12	9.57E-13	8.86E-12
348	7.68E-14	3.74E-12	3.86E-12	1.42E-12	1.08E-12	1.02E-11
353	7.84E-14	3.88E-12	4.04E-12	1.54E-12	1.12E-12	1.07E-11
363	8.16E-14	4.17E-12	4.42E-12	1.81E-12	1.21E-12	1.17E-11
368	8.32E-14	4.32E-12	4.63E-12	1.95E-12	1.26E-12	1.22E-11
375	8.56E-14	4.54E-12	4.93E-12	2.17E-12	1.32E-12	1.30E-11
400	9.48E-14	5.4E-12	6.19E-12	3.11E-12	1.59E-12	1.64E-11
430	1.07E-13	6.57E-12	8.13E-12	4.58E-12	1.95E-12	2.13E-11
500	1.44E-13	1.0E-11	1.51E-11	9.89E-12	3.02E-12	3.82E-11
600	2.15E-13	1.69E-11	3.45E-11	2.33E-11	5.21E-12	8.01E-11
700	3.14E-13	2.65E-11	7.13E-11	4.54E-11	8.3E-12	1.52E-10
800	4.48E-13	3.92E-11	1.34E-10	7.76E-11	1.25E-11	2.64E-10
900	6.21E-13	5.53E-11	2.33E-10	1.21E-10	1.79E-11	4.28E-10
1000	8.42E-13	7.5E-11	3.75E-10	1.77E-10	2.47E-11	6.53E-10

Table S3. Calculated individual and total CVT/SCT rate constants versus 1000/T for reactions of C_6Br_5OH with·OH radical within 200-1000 K.

T (K)	k_{C1}	k_{C2}	k_{C3}	k_{C4}	k_{C5}	k_{C}
200	6.6E-14	7.24E-13	5.22E-13	4.78E-14	8.29E-15	1.37E-12
220	6.68E-14	1.06E-12	7.57E-13	9.68E-14	2.72E-14	2.01E-12
240	6.83E-14	1.48E-12	1.05E-12	1.8E-13	7.78E-14	2.86E-12
250	6.92E-14	1.72E-12	1.23E-12	2.4E-13	1.25E-13	3.38E-12
253	6.95E-14	1.8E-12	1.28E-12	2.6E-13	1.44E-13	3.55E-12
268	7.12E-14	2.22E-12	1.58E-12	3.83E-13	2.76E-13	4.53E-12
283	7.32E-14	2.69E-12	1.91E-12	5.46E-13	5.02E-13	5.72E-12
296	7.5E-14	3.15E-12	2.23E-12	7.25E-13	8.09E-13	6.99E-12
298	7.53E-14	3.22E-12	2.28E-12	7.56E-13	8.68E-13	7.20E-12
313	7.77E-14	3.81E-12	2.69E-12	1.02E-12	1.44E-12	9.04E-12
328	8.03E-14	4.45E-12	3.14E-12	1.35E-12	2.29E-12	1.13E-11
331	8.08E-14	4.58E-12	3.24E-12	1.43E-12	2.5E-12	1.18E-11
333	8.12E-14	4.68E-12	3.3E-12	1.48E-12	2.65E-12	1.22E-11
348	8.4E-14	5.4E-12	3.81E-12	1.9E-12	4.04E-12	1.52E-11
353	8.5E-14	5.71E-12	3.99E-12	2.06E-12	4.62E-12	1.65E-11
363	8.7E-14	6.18E-12	4.36E-12	2.41E-12	5.98E-12	1.90E-11
368	8.81E-14	6.45E-12	4.55E-12	2.6E-12	6.77E-12	2.05E-11
375	8.96E-14	6.85E-12	4.82E-12	2.88E-12	8.03E-12	2.27E-11
400	9.53E-14	8.36E-12	5.89E-12	4.07E-12	1.41E-11	3.25E-11
430	1.03E-13	1.04E-11	7.33E-12	5.92E-12	2.59E-11	4.97E-11
500	1.24E-13	1.61E-11	1.14E-11	1.24E-11	8.36E-11	1.24E-10
600	1.62E-13	2.67E-11	1.93E-11	2.83E-11	2.99E-10	3.73E-10
700	2.12E-13	4.03E-11	2.99E-11	5.45E-11	7.89E-10	9.14E-10
800	2.75E-13	5.68E-11	4.34E-11	9.36E-11	1.71E-9	1.90E-9
900	3.53E-13	7.63E-11	6.03E-11	1.48E-10	3.23E-9	3.51E-9
1000	4.49E-13	9.92E-11	8.09E-11	2.19E-10	5.52E-9	5.92E-9

Table S4. Branching ratios of k_{A1}/k_A~k_{A5}/k_A at 200-1000 K.

T (K)	k_{A1}/k_A	k_{A2}/k_A	k_{A3}/k_A	k_{A4}/k_A	k_{A5}/k_A
200	2.36%	39.79%	10.28%	9.64%	37.93%
220	1.97%	43.26%	11.56%	10.66%	32.55%
240	1.60%	45.31%	14.79%	11.19%	27.12%
250	1.43%	46.02%	16.38%	11.34%	24.83%
253	1.38%	46.12%	17.04%	11.33%	24.13%
268	1.20%	47.96%	17.62%	11.62%	21.59%
283	1.03%	48.40%	19.91%	11.61%	19.05%
296	0.90%	48.59%	21.89%	11.54%	17.08%
298	0.89%	48.57%	22.18%	11.53%	16.84%
313	0.77%	48.64%	24.05%	11.42%	15.13%
328	0.67%	48.62%	25.79%	11.29%	13.63%
331	0.66%	48.57%	26.16%	11.32%	13.30%
333	0.64%	48.50%	26.40%	11.27%	13.20%
348	0.57%	48.44%	27.91%	11.13%	11.95%
353	0.55%	48.34%	28.45%	11.07%	11.59%
363	0.51%	48.15%	29.37%	10.99%	10.99%
368	0.49%	48.09%	29.79%	10.97%	10.67%
375	0.46%	47.97%	30.41%	10.92%	10.23%
400	0.39%	47.49%	32.39%	10.69%	9.05%
430	0.33%	46.91%	34.34%	10.51%	7.92%
500	0.23%	45.54%	37.95%	10.14%	6.15%
600	0.16%	43.54%	41.56%	9.95%	4.79%
700	0.13%	42.02%	43.94%	9.89%	4.03%
800	0.11%	40.76%	45.68%	9.90%	3.56%
900	0.10%	39.63%	46.97%	10.05%	3.26%
1000	0.09%	38.55%	48.19%	10.12%	3.05%

Table S5. Branching ratios of k_{B1}/k_B~k_{B5}/k_B at 200-1000 K.

T (K)	k_{B1}/k_B	k_{B2}/k_B	k_{B3}/k_B	k_{B4}/k_B	k_{B5}/k_B
200	1.80%	45.53%	37.52%	3.86%	11.29%
220	1.59%	44.35%	38.41%	4.28%	11.37%
240	1.41%	43.31%	38.82%	5.05%	11.41%
250	1.33%	42.89%	38.77%	5.57%	11.44%
253	1.30%	42.66%	38.89%	5.75%	11.41%
268	1.19%	41.88%	38.79%	6.73%	11.41%
283	1.09%	41.03%	38.69%	7.86%	11.34%
296	1.01%	40.35%	38.44%	8.96%	11.24%
298	1.00%	40.19%	38.47%	9.13%	11.21%
313	0.92%	39.22%	38.26%	10.54%	11.07%
328	0.84%	38.22%	38.11%	11.95%	10.88%
331	0.83%	37.96%	38.07%	12.31%	10.84%
333	0.82%	37.81%	38.04%	12.53%	10.80%
348	0.76%	36.75%	37.93%	13.95%	10.61%
353	0.74%	36.40%	37.90%	14.45%	10.51%
363	0.70%	35.67%	37.81%	15.48%	10.35%
368	0.68%	35.29%	37.82%	15.93%	10.29%
375	0.66%	34.80%	37.79%	16.63%	10.12%
400	0.58%	32.96%	37.78%	18.98%	9.70%
430	0.50%	30.79%	38.10%	21.47%	9.14%
500	0.38%	26.21%	39.58%	25.92%	7.92%
600	0.27%	21.09%	43.06%	29.08%	6.50%
700	0.21%	17.46%	46.97%	29.91%	5.47%
800	0.17%	14.86%	50.81%	29.42%	4.74%
900	0.15%	12.93%	54.46%	28.28%	4.18%
1000	0.13%	11.49%	57.47%	27.13%	3.79%

Table S6. Branching ratios of k_{C1}/k_C~k_{C5}/k_C at 200-1000 K.

T (K)	k_{C1}/k_{CT}	k_{C2}/k_{CT}	k_{C3}/k_{CT}	k_{C4}/k_{CT}	k_{C5}/k_{CT}
200	4.82%	52.92%	38.16%	3.49%	0.61%
220	3.33%	52.79%	37.70%	4.82%	1.36%
240	2.39%	51.82%	36.76%	6.30%	2.72%
250	2.05%	50.82%	36.35%	7.09%	3.69%
253	1.96%	50.65%	36.02%	7.32%	4.05%
268	1.57%	49.00%	34.88%	8.45%	6.09%
283	1.28%	47.02%	33.39%	9.54%	8.77%
296	1.07%	45.07%	31.91%	10.37%	11.58%
298	1.05%	44.73%	31.67%	10.50%	12.06%
313	0.86%	42.16%	29.76%	11.29%	15.93%
328	0.71%	39.35%	27.76%	11.94%	20.25%
331	0.68%	38.71%	27.39%	12.09%	21.13%
333	0.67%	38.39%	27.07%	12.14%	21.74%
348	0.55%	35.45%	25.01%	12.47%	26.52%
353	0.52%	34.68%	24.23%	12.51%	28.06%
363	0.46%	32.50%	22.93%	12.67%	31.45%
368	0.43%	31.53%	22.24%	12.71%	33.09%
375	0.40%	30.22%	21.26%	12.70%	35.42%
400	0.29%	25.71%	18.12%	12.52%	43.36%
430	0.21%	20.95%	14.76%	11.92%	52.16%
500	0.10%	13.02%	9.22%	10.03%	67.62%
600	0.04%	7.15%	5.17%	7.58%	80.06%
700	0.02%	4.41%	3.27%	5.96%	86.33%
800	0.01%	2.98%	2.28%	4.92%	89.81%
900	0.01%	2.17%	1.72%	4.21%	91.89%
1000	0.01%	1.68%	1.37%	3.70%	93.25%

Table S7. Calculated atmospheric lifetime (τ) values for C_6F_5OH determined by ·OH at different temperature (*T*) and altitude (*H*) in the earth atmosphere according to the rate constants (k_A).

[a][·OH] [b]τ *T* (K)	k_A	*H* (km)	9.0E+05	9.7E+05	1.0E+06	1.50E+06	2.0E+06	3.0E+06	5.0E+06	1.0E+07	1.5E+07
216.69	2.36E-12	12	130.78	121.34	117.70	78.47	58.85	39.23	23.54	11.77	7.85
223.29	2.58E-12	10	119.63	111.00	107.67	71.78	53.83	35.89	21.53	10.77	7.18
229.78	2.84E-12	9	108.68	100.83	97.81	65.21	48.90	32.60	19.56	9.78	6.52
236.27	3.13E-12	8	98.61	91.49	88.75	59.16	44.37	29.58	17.75	8.87	5.92
242.76	3.44E-12	7	89.72	83.25	80.75	53.83	40.37	26.92	16.15	8.07	5.38
249.25	3.80E-12	6	81.22	75.36	73.10	48.73	36.55	24.37	14.62	7.31	4.87
255.74	4.18E-12	5	73.84	68.51	66.45	44.30	33.23	22.15	13.29	6.65	4.43
262.23	3.92E-12	4	78.74	73.05	70.86	47.24	35.43	23.62	14.17	7.09	4.72
268.72	4.27E-12	3	72.28	67.07	65.05	43.37	32.53	21.68	13.01	6.51	4.34
275.21	4.65E-12	2	66.37	61.58	59.74	39.82	29.87	19.91	11.95	5.97	3.98
281.70	5.05E-12	1	61.12	56.71	55.01	36.67	27.50	18.34	11.00	5.50	3.67
288.19	5.47E-12	0	56.42	52.35	50.78	33.85	25.39	16.93	10.16	5.08	3.39
298.15	6.20E-12	0	49.78	46.19	44.80	29.87	22.40	14.93	8.96	4.48	2.99

[a]Herein, the [·OH] is from references [66,67] (unit: molecule cm^{-3}); [b] Unit: *h*

Table S8. Calculated atmospheric lifetime (τ) values for C_6Cl_5OH determined by ·OH at different temperature (*T*) and altitude (*H*) in the earth atmosphere according to the rate constants (k_B).

[a][•OH] [b]τ *T* (K)	k_B	*H* (km)	9.0E+05	9.7E+05	1.0E+06	1.50E+06	2.0E+06	3.0E+06	5.0E+06	1.0E+07	1.5E+07
216.69	3.12E-12	12	98.92	91.78	89.03	59.35	44.52	29.68	17.81	8.90	5.94
223.29	3.28E-12	10	94.10	87.31	84.69	56.46	42.34	28.23	16.94	8.47	5.65
229.78	3.47E-12	9	88.95	82.53	80.05	53.37	40.03	26.68	16.01	8.01	5.34
236.27	3.66E-12	8	84.33	78.24	75.90	50.60	37.95	25.30	15.18	7.59	5.06
242.76	3.87E-12	7	79.75	74.00	71.78	47.85	35.89	23.93	14.36	7.18	4.79
249.25	4.10E-12	6	75.28	69.85	67.75	45.17	33.88	22.58	13.55	6.78	4.52
255.74	4.35E-12	5	70.95	65.83	63.86	42.57	31.93	21.29	12.77	6.39	4.26
262.23	4.60E-12	4	67.10	62.25	60.39	40.26	30.19	20.13	12.08	6.04	4.03
268.72	4.87E-12	3	63.38	58.80	57.04	38.03	28.52	19.01	11.41	5.70	3.80
275.21	5.18E-12	2	59.58	55.28	53.63	35.75	26.81	17.88	10.73	5.36	3.58
281.70	5.49E-12	1	56.22	52.16	50.60	33.73	25.30	16.87	10.12	5.06	3.37
288.19	5.83E-12	0	52.94	49.12	47.65	31.76	23.82	15.88	9.53	4.76	3.18
298.15	6.40E-12	0	48.23	44.75	43.40	28.94	21.70	14.47	8.68	4.34	2.89

[a]Herein, the [•OH] is from references [66,67] (unit: molecule cm^{-3}); [b] Unit: *h*

Table S9. Calculated atmospheric lifetime (τ) values for C_6Br_5OH determined by ·OH at different temperature (*T*) and altitude (*H*) in the earth atmosphere according to the rate constants (k_C).

[a][·OH] [b]τ *T* (K)	k_C	*H* (km)	9.0E+05	9.7E+05	1.0E+06	1.50E+06	2.0E+06	3.0E+06	5.0E+06	1.0E+07	1.5E+07
216.69	1.89E-12	12	163.30	151.52	146.97	97.98	73.49	48.99	29.39	14.70	9.80
223.29	2.13E-12	10	144.90	134.45	130.41	86.94	65.21	43.47	26.08	13.04	8.69
229.78	2.39E-12	9	129.14	119.82	116.23	77.48	58.11	38.74	23.25	11.62	7.75
236.27	2.68E-12	8	115.16	106.85	103.65	69.10	51.82	34.55	20.73	10.36	6.91
242.76	2.99E-12	7	103.22	95.78	92.90	61.93	46.45	30.97	18.58	9.29	6.19
249.25	3.34E-12	6	92.41	85.74	83.17	55.44	41.58	27.72	16.63	8.32	5.54
255.74	3.71E-12	5	83.19	77.19	74.87	49.92	37.44	24.96	14.97	7.49	4.99
262.23	4.13E-12	4	74.73	69.34	67.26	44.84	33.63	22.42	13.45	6.73	4.48
268.72	4.58E-12	3	67.39	62.53	60.65	40.43	30.33	20.22	12.13	6.07	4.04
275.21	5.07E-12	2	60.88	56.48	54.79	36.53	27.39	18.26	10.96	5.48	3.65
281.70	5.61E-12	1	55.02	51.05	49.51	33.01	24.76	16.50	9.90	4.95	3.30
288.19	6.20E-12	0	49.78	46.19	44.80	29.87	22.40	14.93	8.96	4.48	2.99
298.15	7.21E-12	0	42.81	39.72	38.53	25.68	19.26	12.84	7.71	3.85	2.57

[a]Herein, the [·OH] is from references [66,67] (unit: molecule cm^{-3}); [b] Unit: *h*

Table S10. The free energies barriers (in kcal/mol) for the degradation of C_6F_5OH in the absence and presence of $(TiO_2)_n$ (*n* = 4, 6, 8, 12, and 16) clusters obtained at the M06-2X/6-311++G(3df,3pd)-LANL2DZ level based on the optimized geometries at the levels of M06-2X/6-311G(d,p)-LANL2DZ for *n*=4, 6, 8, 12 and M06-2X/6-31G(d)-LANL2DZ for n=16 .

Reactions	Naked	$(TiO_2)_4$	$(TiO_2)_6$	$(TiO_2)_8$	$(TiO_2)_{12}$	$(TiO_2)_{16}$
RA1 or RA1-$(TiO_2)_n$	8.78	4.95	4.67	3.50	4.32	3.14
RA2 or RA2-$(TiO_2)_n$	9.98	7.51	6.29	4.00	6.73	5.84
RA3 or RA3-$(TiO_2)_n$	9.50	10.35	9.54	9.92	10.56	9.05
RA4 or RA4-$(TiO_2)_n$	11.23	12.23	12.07	11.50	11.59	11.69
RA5 or RA5-$(TiO_2)_n$	10.22	11.59	12.69	11.20	11.67	12.17

Table S11. Calculated individual and total rate constants for reactions of C_6F_5OH with ·OH radical within 200−430 K by TST method.

T (K)	k_{A1}	k_{A2}	k_{A3}	k_{A4}	k_{A5}	k_A
200	5.22E-20	1.68E-16	9.10E-17	8.45E-18	5.67E-17	3.24E-16
220	1.73E-19	2.35E-16	1.34E-16	1.52E-17	8.73E-17	4.72E-16
240	4.64E-19	3.15E-16	1.86E-16	2.52E-17	1.27E-16	6.54E-16
250	7.17E-19	3.58E-16	2.14E-16	3.15E-17	1.50E-16	7.54E-16
253	8.16E-19	3.73E-16	2.24E-16	3.37E-17	1.57E-16	7.89E-16
268	1.45E-18	4.46E-16	2.74E-16	4.55E-17	1.97E-16	9.64E-16
283	2.41E-18	5.25E-16	3.29E-16	6.00E-17	2.42E-16	1.16E-15
296	3.63E-18	5.98E-16	3.81E-16	7.44E-17	2.84E-16	1.34E-15
298	3.84E-18	6.09E-16	3.89E-16	7.66E-17	2.91E-16	1.37E-15
313	5.81E-18	7.03E-16	4.55E-16	9.65E-17	3.46E-16	1.61E-15
328	8.53E-18	7.95E-16	5.24E-16	1.19E-16	4.06E-16	1.85E-15
331	9.16E-18	8.19E-16	5.41E-16	1.24E-16	4.21E-16	1.91E-15
333	9.59E-18	8.30E-16	5.47E-16	1.27E-16	4.29E-16	1.94E-15
348	1.34E-17	9.32E-16	6.24E-16	1.54E-16	4.94E-16	2.22E-15
353	1.49E-17	9.69E-16	6.50E-16	1.64E-16	5.20E-16	2.32E-15
363	1.82E-17	1.04E-15	7.06E-16	1.84E-16	5.69E-16	2.52E-15
368	2.02E-17	1.08E-15	7.34E-16	1.94E-16	5.90E-16	2.62E-15
375	2.30E-17	1.13E-15	7.74E-16	2.09E-16	6.25E-16	2.76E-15
400	3.54E-17	1.33E-15	9.23E-16	2.71E-16	7.63E-16	3.32E-15
430	5.56E-17	1.57E-15	1.11E-15	3.55E-16	9.40E-16	4.03E-15

Table S12. Calculated individual and total rate constants for reactions of C_6F_5OH with ·OH radical catalyzed by $(TiO_2)_4$ cluster within 200−430 K.

T (K)	$k_{\text{A1-(TiO2)4}}$	$k_{\text{A2-(TiO2)4}}$	$k_{\text{A3-(TiO2)4}}$	$k_{\text{A4-(TiO2)4}}$	$k_{\text{A5-(TiO2)4}}$	$k_{\text{A-(TiO2)4}}$
200	4.34E-04	7.14E-12	1.71E-15	1.03E-18	6.08E-18	4.34E-04
220	3.92E-05	4.20E-12	2.61E-15	2.14E-18	1.04E-17	3.92E-05
240	5.32E-06	2.74E-12	3.78E-15	3.99E-18	1.65E-17	5.32E-06
250	2.20E-06	2.29E-12	4.48E-15	5.27E-18	2.03E-17	2.20E-06
253	1.72E-06	2.17E-12	4.71E-15	5.71E-18	2.14E-17	1.72E-06
268	5.38E-07	1.72E-12	5.93E-15	8.27E-18	2.83E-17	5.38E-07
283	1.91E-07	1.40E-12	7.34E-15	1.16E-17	3.63E-17	1.91E-07
296	8.49E-08	1.20E-12	8.72E-15	1.51E-17	4.42E-17	8.49E-08
298	7.55E-08	1.17E-12	8.95E-15	1.57E-17	4.56E-17	7.55E-08
313	3.27E-08	1.01E-12	1.08E-14	2.07E-17	5.62E-17	3.27E-08
328	1.53E-08	8.78E-13	1.28E-14	2.68E-17	6.81E-17	1.53E-08
331	1.32E-08	8.56E-13	1.32E-14	2.82E-17	7.07E-17	1.32E-08
333	1.21E-08	8.42E-13	1.35E-14	2.92E-17	7.25E-17	1.21E-08
348	6.19E-09	7.52E-13	1.58E-14	3.65E-17	8.64E-17	6.19E-09
353	5.02E-09	7.26E-13	1.67E-14	3.93E-17	9.10E-17	5.02E-09
363	3.37E-09	6.79E-13	1.84E-14	4.54E-17	1.01E-16	3.37E-09
368	2.77E-09	6.59E-13	1.93E-14	4.86E-17	1.07E-16	2.77E-09
375	2.14E-09	6.32E-13	2.06E-14	5.32E-17	1.15E-16	2.14E-09
400	9.12E-10	5.55E-13	2.57E-14	7.22E-17	1.44E-16	9.13E-10
430	3.75E-10	4.90E-13	3.28E-14	1.00E-16	1.86E-16	3.76E-10

Table S13. Calculated individual and total rate constants for reactions of C_6F_5OH with ·OH radical catalyzed by $(TiO_2)_6$ cluster within 200−430 K.

T (K)	$k_{\mathrm{A1\text{-}(TiO2)6}}$	$k_{\mathrm{A2\text{-}(TiO2)6}}$	$k_{\mathrm{A3\text{-}(TiO2)6}}$	$k_{\mathrm{A4\text{-}(TiO2)6}}$	$k_{\mathrm{A5\text{-}(TiO2)6}}$	$k_{\mathrm{A\text{-}(TiO2)6}}$
200	3.39E-04	6.89E-19	7.48E-15	1.31E-18	4.52E-19	3.39E-04
220	2.93E-05	1.88E-18	8.91E-15	2.75E-18	9.52E-19	2.93E-05
240	3.82E-06	4.40E-18	1.05E-14	5.18E-18	1.79E-18	3.82E-06
250	1.57E-06	6.44E-18	1.13E-14	6.84E-18	2.37E-18	1.57E-06
253	1.21E-06	7.18E-18	1.16E-14	7.41E-18	2.57E-18	1.21E-06
268	3.75E-07	1.20E-17	1.30E-14	1.08E-17	3.73E-18	3.75E-07
283	1.30E-07	1.91E-17	1.44E-14	1.52E-17	5.25E-18	1.30E-07
296	5.68E-08	2.76E-17	1.57E-14	1.99E-17	6.87E-18	5.68E-08
298	5.02E-08	2.91E-17	1.59E-14	2.06E-17	7.15E-18	5.02E-08
313	2.15E-08	4.29E-17	1.76E-14	2.74E-17	9.48E-18	2.15E-08
328	9.94E-09	6.13E-17	1.93E-14	3.55E-17	1.23E-17	9.94E-09
331	8.56E-09	6.56E-17	1.96E-14	3.73E-17	1.29E-17	8.56E-09
333	7.80E-09	6.86E-17	1.99E-14	3.85E-17	1.33E-17	7.80E-09
348	3.96E-09	9.46E-17	2.17E-14	4.87E-17	1.68E-17	3.96E-09
353	3.19E-09	1.05E-16	2.23E-14	5.24E-17	1.81E-17	3.19E-09
363	2.12E-09	1.28E-16	2.36E-14	6.04E-17	2.09E-17	2.12E-09
368	1.75E-09	1.40E-16	2.43E-14	6.47E-17	2.24E-17	1.75E-09
375	1.34E-09	1.60E-16	2.52E-14	7.09E-17	2.46E-17	1.34E-09
400	5.64E-10	2.46E-16	2.87E-14	9.67E-17	3.35E-17	5.64E-10
430	2.28E-10	3.89E-16	3.32E-14	1.35E-16	4.65E-17	2.28E-10

Table S14. Calculated individual and total rate constants for reactions of C_6F_5OH with ·OH radical catalyzed by $(TiO_2)_8$ cluster within 200−430 K.

T (K)	$k_{\mathrm{A1\text{-}(TiO2)8}}$	$k_{\mathrm{A2\text{-}(TiO2)8}}$	$k_{\mathrm{A3\text{-}(TiO2)8}}$	$k_{\mathrm{A4\text{-}(TiO2)8}}$	$k_{\mathrm{A5\text{-}(TiO2)8}}$	$k_{\mathrm{A\text{-}(TiO2)8}}$
200	7.24E-04	6.01E-19	4.34E-15	5.79E-18	1.18E-17	7.24E-04
220	6.89E-05	2.03E-18	6.22E-15	1.04E-17	1.99E-17	6.89E-05
240	9.86E-06	5.68E-18	8.54E-15	1.70E-17	3.12E-17	9.86E-06
250	4.19E-06	8.98E-18	9.87E-15	2.12E-17	3.82E-17	4.19E-06
253	3.28E-06	1.02E-17	1.03E-14	2.26E-17	4.04E-17	3.28E-06
268	1.06E-06	1.90E-17	1.26E-14	3.04E-17	5.30E-17	1.06E-06
283	3.88E-07	3.32E-17	1.52E-14	3.97E-17	6.79E-17	3.88E-07
296	1.76E-07	5.16E-17	1.76E-14	4.94E-17	8.24E-17	1.76E-07
298	1.56E-07	5.50E-17	1.80E-14	5.09E-17	8.46E-17	1.56E-07
313	6.94E-08	8.75E-17	2.12E-14	6.38E-17	1.04E-16	6.94E-08
328	3.31E-08	1.34E-16	2.46E-14	7.82E-17	1.25E-16	3.31E-08
331	2.88E-08	1.45E-16	2.54E-14	8.17E-17	1.31E-16	2.88E-08
333	2.63E-08	1.53E-16	2.59E-14	8.35E-17	1.33E-16	2.63E-08
348	1.37E-08	2.25E-16	2.98E-14	1.01E-16	1.58E-16	1.37E-08
353	1.12E-08	2.54E-16	3.12E-14	1.07E-16	1.67E-16	1.12E-08
363	7.56E-09	3.21E-16	3.40E-14	1.20E-16	1.86E-16	7.56E-09
368	6.28E-09	3.59E-16	3.55E-14	1.27E-16	1.96E-16	6.28E-09
375	4.88E-09	4.18E-16	3.76E-14	1.37E-16	2.10E-16	4.88E-09
400	2.14E-09	6.96E-16	4.59E-14	1.76E-16	2.64E-16	2.14E-09
430	9.05E-10	1.20E-15	5.71E-14	2.29E-16	3.38E-16	9.05E-10

Table S15. Calculated individual and total rate constants for reactions of C_6F_5OH with ·OH radical catalyzed by $(TiO_2)_{12}$ cluster within 200−430 K.

T (K)	$k_{A1\text{-}(TiO2)12}$	$k_{A2\text{-}(TiO2)12}$	$k_{A3\text{-}(TiO2)12}$	$k_{A4\text{-}(TiO2)12}$	$k_{A5\text{-}(TiO2)12}$	$k_{A\text{-}(TiO2)12}$
200	1.44E-04	2.02E-16	1.23E-15	3.81E-18	3.14E-18	1.44E-04
220	1.36E-05	3.82E-16	1.84E-15	7.41E-18	6.19E-18	1.36E-05
240	1.90E-06	6.63E-16	2.60E-15	1.30E-17	1.11E-17	1.90E-06
250	8.01E-07	8.50E-16	3.05E-15	1.67E-17	1.42E-17	8.01E-07
253	6.27E-07	9.13E-16	3.19E-15	1.80E-17	1.54E-17	6.27E-07
268	2.01E-07	1.28E-15	3.97E-15	2.52E-17	2.17E-17	2.01E-07
283	7.26E-08	1.74E-15	4.86E-15	3.43E-17	2.97E-17	7.26E-08
296	3.27E-08	2.22E-15	5.71E-15	4.36E-17	3.80E-17	3.27E-08
298	2.91E-08	2.30E-15	5.86E-15	4.50E-17	3.95E-17	2.91E-08
313	1.28E-08	2.99E-15	6.97E-15	5.84E-17	5.12E-17	1.28E-08
328	6.07E-09	3.81E-15	8.22E-15	7.38E-17	6.47E-17	6.07E-09
331	5.27E-09	3.99E-15	8.48E-15	7.71E-17	6.81E-17	5.27E-09
333	4.82E-09	4.11E-15	8.65E-15	7.94E-17	7.01E-17	4.82E-09
348	2.48E-09	5.12E-15	1.01E-14	9.79E-17	8.67E-17	2.48E-09
353	2.03E-09	5.50E-15	1.06E-14	1.05E-16	9.33E-17	2.03E-09
363	1.37E-09	6.29E-15	1.16E-14	1.19E-16	1.06E-16	1.37E-09
368	1.13E-09	6.72E-15	1.22E-14	1.27E-16	1.13E-16	1.13E-09
375	8.81E-10	7.35E-15	1.29E-14	1.38E-16	1.23E-16	8.81E-10
400	3.81E-10	9.92E-15	1.60E-14	1.83E-16	1.64E-16	3.81E-10
430	1.60E-10	1.37E-14	2.02E-14	2.46E-16	2.23E-16	1.60E-10

Table S16. Calculated individual and total rate constants for reactions of C_6F_5OH with ·OH radical catalyzed by $(TiO_2)_{16}$ cluster within 200−430 K.

T (K)	$k_{A1\text{-}(TiO2)16}$	$k_{A2\text{-}(TiO2)16}$	$k_{A3\text{-}(TiO2)16}$	$k_{A4\text{-}(TiO2)16}$	$k_{A5\text{-}(TiO2)16}$	$k_{A\text{-}(TiO2)16}$
200	1.32E-05	2.67E-16	8.87E-15	3.33E-18	1.11E-18	1.32E-05
220	1.62E-06	5.42E-16	1.10E-14	6.44E-18	2.33E-18	1.62E-06
240	2.84E-07	9.93E-16	1.34E-14	1.12E-17	4.34E-18	2.84E-07
250	1.32E-07	1.30E-15	1.47E-14	1.44E-17	5.72E-18	1.32E-07
253	1.06E-07	1.41E-15	1.51E-14	1.55E-17	6.19E-18	1.06E-07
268	3.87E-08	2.04E-15	1.72E-14	2.16E-17	8.97E-18	3.87E-08
283	1.57E-08	2.85E-15	1.95E-14	2.93E-17	1.26E-17	1.57E-08
296	7.78E-09	3.73E-15	2.16E-14	3.71E-17	1.64E-17	7.78E-09
298	7.00E-09	3.88E-15	2.19E-14	3.84E-17	1.70E-17	7.00E-09
313	3.39E-09	5.16E-15	2.45E-14	4.95E-17	2.25E-17	3.39E-09
328	1.76E-09	6.71E-15	2.72E-14	6.25E-17	2.92E-17	1.76E-09
331	1.54E-09	7.05E-15	2.78E-14	6.53E-17	3.06E-17	1.54E-09
333	1.43E-09	7.29E-15	2.81E-14	6.70E-17	3.15E-17	1.43E-09
348	7.98E-10	9.26E-15	3.11E-14	8.27E-17	3.98E-17	7.98E-10
353	6.65E-10	9.98E-15	3.21E-14	8.83E-17	4.25E-17	6.65E-10
363	4.70E-10	1.16E-14	3.42E-14	1.01E-16	4.93E-17	4.70E-10
368	3.99E-10	1.24E-14	3.52E-14	1.06E-16	5.25E-17	3.99E-10
375	3.19E-10	1.37E-14	3.68E-14	1.16E-16	5.75E-17	3.19E-10
400	1.52E-10	1.89E-14	4.25E-14	1.53E-16	7.81E-17	1.52E-10
430	7.05E-11	2.68E-14	5.00E-14	2.06E-16	1.08E-16	7.06E-11

Table S17. The relative Gibbs free energies (Δ*G*, in kcal/mol) for the reaction complexes, Gibbs free energies barriers (G_a, in kcal/mol), rate constant (*k*, in cm^3 molecule^{-1} s^{-1}), and branching ratio (*Γ*) at 298 K involving in the H-abstraction channel of C_6F_5OH under the absence and presence of $(TiO_2)_n$ (*n* = 4, 6, 8, 12, and 16) clusters accompanying with the maximum interatomic distance (MID, in nm) obtained at the M06-2X/6-311++G(3df,3pd)-LANL2DZ level based on the optimized geometries at the levels of M06-2X/6-311G(d,p)-LANL2DZ for *n*=4, 6, 8, 12 and M06-2X/6-31G(d)-LANL2DZ for *n*=16 .

Reactions	MID	Δ*G*	G_a	*k*	*Γ*
Naked reaction		2.68	8.78	3.84×10^{-18}	0.28%
$(TiO_2)_4$-catalysis	0.532	-5.78	4.95	7.55×10^{-8}	
$(TiO_2)_6$-catalysis	0.820	-5.26	4.67	5.02×10^{-8}	
$(TiO_2)_8$-catalysis	0.964	-4.79	3.50	1.56×10^{-7}	100%
$(TiO_2)_{12}$-catalysis	1.224	-4.57	4.32	2.91×10^{-8}	
$(TiO_2)_{16}$-catalysis	1.486	-2.56	3.14	7.00×10^{-9}	

Table S18. Eoctoxicity towards aquatic organisms of C_6X_5OH (X=F, Cl, and Br) as well as the eoctoxicity of transformation products of C_6F_5OH. (unit: mg/L)

	Acute toxicity[a] (mg/L)			Chronic toxicity (ChV)[b] (mg/L)			Classification
	LC_{50}>100 or EC_{50}>100			**ChV>10**			Not harmful
	10< LC_{50} (or EC_{50}) <100			**1< ChV <10**			Harmful
	1< LC_{50} (or EC_{50}) <10			**0.1< ChV <1**			Toxic
	LC_{50}<1 or EC_{50}<1			**ChV<0.1**			Very toxic
Compound	Fish (LC_{50})	Daphnid (LC_{50})	Green Algae (EC50)	Fish	Daphnid	Green Algae	ECOSAR Class
C_6F_5OH	12.99	4.92	21.51	1.41	0.94	10.04	Phenols
C_6Cl_5OH	0.39	0.40	1.38	0.06	0.07	0.63	Phenols
C_6Br_5OH	0.08	0.15	0.45	0.02	0.03	0.20	Phenols
IM2A-O-2	4.27	0.58	44.67	0.12	0.03	6.96	Vinyl/Allyl Alcohols
	39.56	25.96	14.19	3.05	2.49	12.45	Ketone alcohols
IM2A-O-4	74.37	1638.40	947.08	6.35	124.58	129.33	Acid Halides
	7.126	0.88	249.36	0.50	0.08	27.50	Vinyl/Allyl Alcohols
P-IM2A-O_2	1237.46	37964.84	19505.76	122.98	2669.10	2307.27	Acid Halides-acid
P-Cy1-1-a	1962.02	464000.00	115000.00	497.69	20128.73	5624.16	Acid Halides
P-Cy1-2-a	145.75	6112.12	2809.80	16.72	399.08	290.24	Acid Halides
P-Cy1-2-b-h	402.09	45186.32	14627.01	72.49	2336.67	985.37	Acid Halides

[a] Criteria set by the European Union (described in Annex VI of Directive 67/548/EEC)

[b] Criteria set by the Chinese hazard evaluation guidelines for new chemical substances (HJ/T 154–2004)